

The Role of Seabed Dynamics In Controlling the Distribution and Preservation of Polycyclic Aromatic Hydrocarbons (PAHs) in Estuarine Sediments

Elizabeth A. Canuel
School of Marine Science/Virginia Institute of Marine Science
Gloucester Point, VA 23062
phone: (804) 684-7134, FAX: (804) 684-7250, e-mail: ecanuel@vims.edu,

Rebecca M. Dickhut (Co-PI)
same address as above
phone: (804) 684-7247, FAX: (804) 684-7250, e-mail: rdickhut@vims.edu

Steven A. Kuehl (Co-PI)
same address as above
phone: (804) 684-7118, FAX: (804) 684-7250, e-mail: kuehl@vims.edu,

Award #N00014-99-1-0125

LONG-TERM GOALS

The overall goal of this study is to examine the role that energy regime and associated seabed dynamics (e.g., frequency and depths of resuspension) play in controlling the distribution of polycyclic aromatic hydrocarbons (PAHs) in estuarine sediments.

OBJECTIVES

Our objectives are to examine sediment PAH distributions in environments representing contrasting depositional regimes within the York River, VA, a sub-estuary of the Chesapeake Bay. Our study utilizes a suite of geochemical tools to quantify sediment processes influencing the distribution of dissolved and solid-phase PAHs. These tools will enable us to quantify particle residence times in surface sediments, determine rates of sediment accumulation and disturbance, and investigate the effects of sediment organic matter composition and diagenesis.

APPROACH

Since PAHs encompass a wide range of physical-chemical properties (e.g., solubility), individual compounds partition to differing degrees between dissolved and solid phases. For example, lower molecular weight compounds with relatively low K_{OW} , and thus decreased affinity for particulate and colloidal organic matter, more readily partition into the interstitial waters than higher molecular weight compounds. Our previous work showed that sediments of the York River, VA estuary were significantly depleted in relatively soluble, low molecular weight PAHs (MW = 128-192) compared with sediments from lower Chesapeake Bay. Since sources of PAHs to sediments of the York River are similar to those for lower Chesapeake Bay (Dickhut et al., 2000), we propose that this observed depletion of low molecular weight PAHs from York River sediments is due to the physically energetic environment of this estuary. In this case, we propose that the increased intensity and frequency of sediment resuspension in the York River promotes loss of relatively soluble, degradable PAHs.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE SEP 2000		2. REPORT TYPE		3. DATES COVERED 00-00-2000 to 00-00-2000	
4. TITLE AND SUBTITLE The Role of Seabed Dynamics In Controlling the Distribution and Preservation of Polycyclic Aromatic Hydrocarbons (PAHs) in Estuarine Sediments				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) School of Marine Science/Virginia Institute of Marine Science,,Gloucester Point,VA,23062				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Frequent physical disturbance can promote degradation of organic matter through the oxygenation of porewaters (e.g., Aller et al., 1996). Consequently, we predict that episodic flushing events associated with storms and periods of increased tidal energy (i.e. neap-spring tidal energy oscillations) will result in renewal of interstitial fluids and exchange of dissolved and/or colloidal associated contaminants with the overlying water column. Given the properties of this compound class, we predict that these processes will preferentially remove, and possibly promote degradation of low MW PAHs and to a lesser extent high MW PAHs.

WORK COMPLETED

Over the past two years, a series of coordinated activities have supported our efforts to quantify the sediment accumulation and disturbance patterns within the York River as well as examine how seabed processes influence sediment PAH distributions. For the sediment processes component of the project, cores were characterized using x-radiography, water content, elemental analysis and radioisotope distributions (Be-7, Pb-210, Cs-137). On the basis of these results, two field studies were undertaken to investigate the effects of seabed mobility on PAH abundance and composition. The field studies were designed to examine: (1) changes in PAH distributions in surface sediments lying along an energy gradient and (2) the effects of depositional regime in promoting PAH diagenesis in sediment cores.

RESULTS

Sediment Dynamics

Four major sub-environments (shoal, flank, secondary channel, and main channel) along a cross-channel transect in the physically dominated upper York River (upstream of Gloucester Point) were characterized using radioisotope geochronology, x-radiographs, and sidescan sonar. Samplings were done on the neap-spring tidal cycle over approximately one year. ^{210}Pb profiles, in conjunction with maximum ^{137}Cs depths, reveal that physical seabed reworking in the four environments is dependent upon multiple forcings (tidal, spring-neap, spring freshet, and storm). The shoal appears to be mostly influenced by the spring-neap tidal cycle with some influence of the April spring freshet (Fig. 1). The adjoining flank, which slopes from the shoal to the secondary channel, is physically mixed to depths of over 150 cm. The mixed layer of the secondary channel varies from 50 to 88 cm, and contains discrete packages of laminated sediments, possibly indicating that the spring freshet and storm cycles predominate the sediment record. The channel exhibits intense physical mixing and was disrupted by Hurricane Floyd (9/16/99) (Fig. 1). Cores collected from the lower York River show the increasing influence of biological mixing towards the mouth. The cross-channel cores taken near the mouth are primarily dominated by biogenic structures and have overall much shallower mixing depths (19-68 cm) than the upper York River.

PAH Distributions in Surface Sediments Collected Along Varying Energy Gradients

In an effort to further explore the influence of physical energy on promoting loss of low molecular weight PAHs from sediments, we collected surface sediments on an along-channel and two across-channel gradients in the York River estuary. These sediments were analyzed for 25 PAHs ranging in MW from 128 to 278 g/mole. We observed little variation in the fraction of low molecular weight PAHs in York River channel sediments (Fig. 2). In contrast, we measured significantly lower fractions of low molecular weight PAHs in the across-channel transects, specifically in sediments

collected on or near the channel flanks subjected to the greatest amount of physical mixing (Fig. 2). In the vicinity of York River – Clay Bank, the flank located on the southwest side of the channel is subjected to the greatest amount of physical mixing due to long-term (based on sediment mixed layers measured using radioisotopes) and short-term (tidal) processes

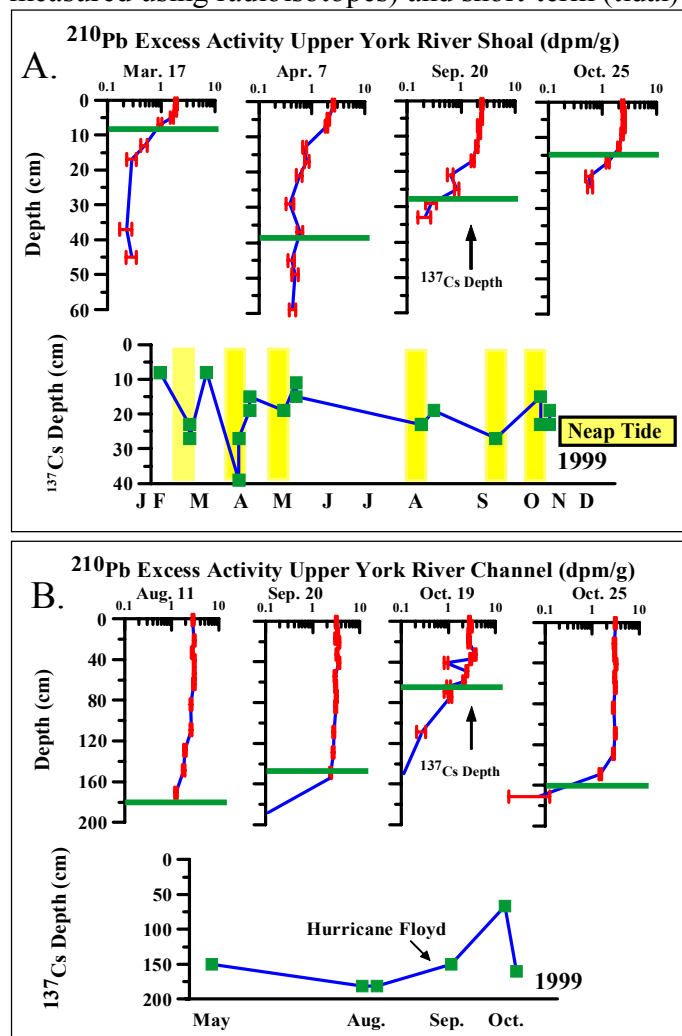


Figure 1. ^{210}Pb profiles and depths of maximum ^{137}Cs penetration for the shoal (A) and channel (B) subenvironments of the upper York River. Mixing depths in the shoal subenvironment (A) appear to be a function of tidal and spring freshet cycles. The decrease in current speed during neap tides may cause deposition of 5 to 30 cm, which is then eroded during the subsequent spring tide. The spring freshet (April 1999) may have contributed to the relatively high deposition observed from March 17 to April 7 as evidenced by the deepening of ^{137}Cs penetration to 40 cm. The sediment profiles indicate that the upper channel subenvironment is subjected to intense physical mixing with mixing depths in excess of 150 cm (B). However, hurricane Floyd disrupted this pattern in mid-September, 1999, causing massive erosion (maximum ^{137}Cs depth reduced to 66 cm in mid-October).

(Dellapenna 1999). At the mouth of the York River, the flank located on the north side of the channel is influenced by the highest degree of physical mixing due to tides and storms (Dellapenna 1999). Our observation of significantly lower fractions of low molecular weight PAHs in the vicinity of these physically mixed flanks compared with channel sediments is consistent with our hypothesis of physically dynamic sediment environments promoting loss/degradation of PAHs.

Role of Physical Mixing on Organic Matter and PAH Diagenesis

The effect of physical energy on the abundance and distribution of PAH was also examined by analysis of sediment cores collected from two locations in the York River: POD and LY. The POD site is characterized by deep (50-100 cm) physical mixing while the LY site is more influenced by biological mixing. Inventories of total pollutant PAH (not including perylene) are similar in the upper 40 cm at both POD and LY. However, below 30 cm, total PAH attenuate more rapidly at the physically dynamic POD site relative to LY (Fig. 3). In addition to differences in total PAH, PAH distributions

within the cores varied compositionally. We propose that the predominance of perylene at depth is due to organic matter diagenesis, which may be enhanced at POD due to the effects of deep physical mixing. Preliminary examination of downcore changes in PAH isomer ratios also suggests that

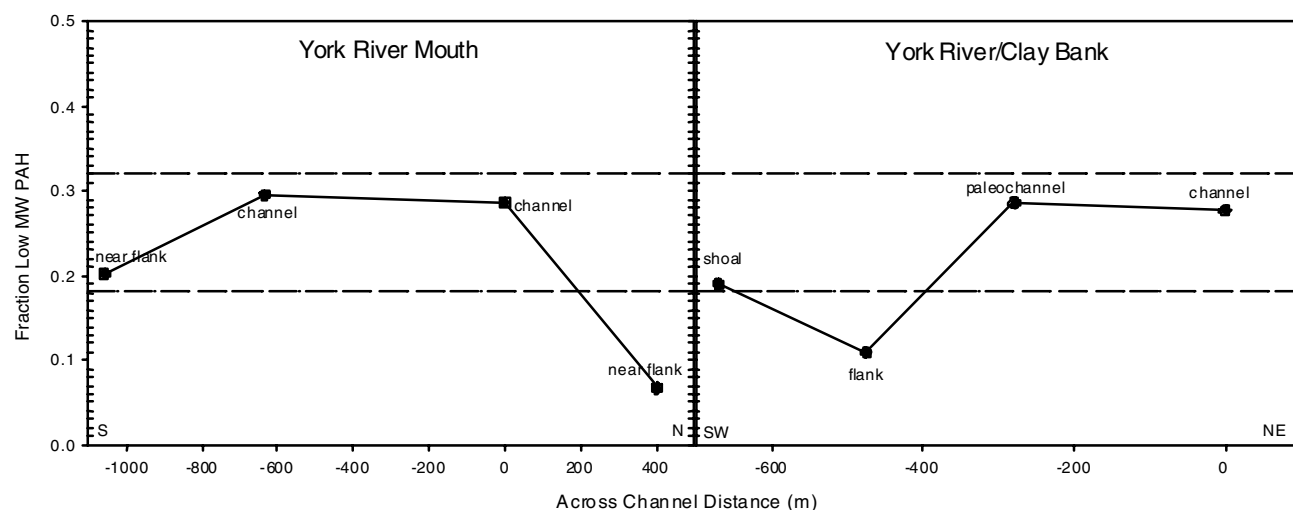


Figure 2. Across channel gradients in fraction of low molecular weight PAHs (MW = 128-192) in York River surface sediments. Dashed lines indicate the 99% confidence intervals for the low molecular weight PAH fraction in York River channel sediments ($n = 13$).

natural attenuation (i.e. microbial degradation) of PAHs may be occurring within sediments collected from POD vs. LY. Ratios of benzo(a)pyrene to benzo(e)pyrene in POD sediments are typical of those found in automobile emissions [B(a)P/B(e)P = 0.3-0.4]. However, at depths of 250 cm we are confident that automobile signatures should be minimal to non-existent and isomer ratios of other PAHs support a coal signature at depth. Thus, lower B(a)P/B(e)P ratios could indicate preferential microbial degradation of B(a)P within the sediment column at the physically reworked POD site. We plan to further investigate the attenuation of this known carcinogen. Future work will also focus on defining the accumulation rates for each core, using isomer ratios to document whether PAH inputs have changed over time, and investigating associations between PAH and different sediment and organic matter fractions.

IMPACT/APPLICATIONS

Our preliminary results shows the influence of physical and biological processes on sediment distributions of PAHs in southern Chesapeake Bay. Results from this study provide insights useful in developing models for predicting contaminant behavior in the environment and assessing the risks PAHs deposited in sediments pose to organisms. These results may also be relevant in developing criteria useful in assessing conditions under which natural attenuation may be a useful remediation strategy.

TRANSITIONS

Results from this study complement other studies funded through the ONR Harbor Processes in the lower Chesapeake Bay and Elizabeth River, VA. Our investigation into the role of physical energy in influencing sediment distributions of PAHs also complements ONR-supported work in the Hudson River estuary (Geyer and colleagues).

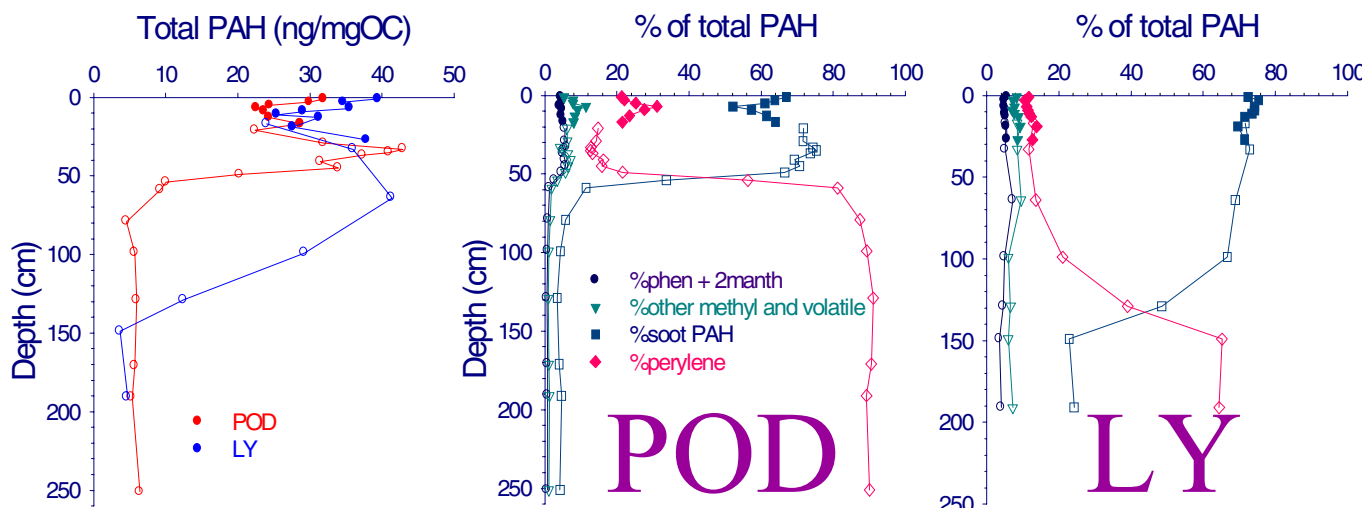


Figure 3. Downcore profiles of total pollutant PAH (not including perylene) and PAH compositional information for sites POD and LY in the York River (Fig. 3). PAH were grouped as follows: %phenanthrene and 2-methylantracene, % other volatile and methyl PAH, %soot PAH and % perylene. Perylene has both a fluvial source (note higher abundance in surface sediments at POD, the more upriver site) and potential diagenetic origin (note higher relative abundances at depth).

RELATED PROJECTS

A research grant funded through VA Sea Grant and EPA (to R.M.D.) supported related work in the urbanized Elizabeth River, VA estuary.

REFERENCES

- Aller, R.C. (1998) Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. *Marine Chemistry* 61: 143-155.
- Dellapenna, T.M., S.A. Kuehl and L.C. Schaffner (1998) Sea-bed mixing and particle residence times in biologically and physically dominated estuarine systems: a comparison of Lower Chesapeake Bay and the York River subestuary. *Est. Coast. Shelf Sci.*, vol. 46, pp 777-795.
- Dellapenna, T. (1999) Fine-scale strata formation in biologically and physically dominated estuarine systems within the lower Chesapeake and York River subestuary. Ph.D. Dissertation, College of William and Mary.

PUBLICATIONS

- Arzayus, K.M., R.M. Dickhut and E.A. Canuel (submitted) Role of atmospheric flux in controlling sedimentary distributions of polycyclic aromatic hydrocarbons (PAHs) in Chesapeake Bay. *ES&T*.
- Dellapenna, T.M., S.A. Kuehl and L. Pitts (submitted) Transient, longitudinal furrows in the York River subestuary, Chesapeake Bay: Furrow evolution and effects on seabed mixing and sediment transport.
- Dickhut, R.M., E.A. Canuel, K.E. Gustafson, K. Liu, Y.M. Arzayus, S.E. Walker, G. Edgecombe, M.O. Gaylor and E.H. Macdonald (2000) Automobiles as sources of polycyclic aromatic hydrocarbons to the Chesapeake Bay. *ES&T*, v. 34.